

Year 2000 R&D status of large-scale lithium ion secondary batteries in the national project of Japan

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Abstract

LIBES has investigated new Ni–Co and Mn cathodes, such as $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ and Li-rich LiMn_2O_4 cathodes, and graphite compound anodes whose performance exceeds that of a single graphite anode, such as graphite–coke, Ag-deposited graphite and graphite-hard carbon anodes, to develop batteries with high capacity, long cycle life, and with less or no content of Co. It has also developed large-scale lithium ion secondary batteries for dispersed energy storage. Parameters such as battery capacity and energy efficiency have already achieved their original targets for both types. Specific power has also reached its target in the battery module level for electric vehicles (EV) purpose. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

As part of the New Sunshine Program promoted by the Agency of Industrial Science and Technology (AIST), MITI, a 10-year project to develop dispersed energy storage technology commenced in FY1992 and will be completed in FY2001. The Lithium Battery Energy Storage Technology Research Association (LIBES) has been entrusted with this challenge by a project-managing agency, the New Energy and Industrial Technology Development Organization (NEDO), and has been conducting research and development. Based on the results of 10 Wh class cell developments in Phase I, the subsequent 5 years, which began in FY1997, were designated as Phase II. As originally planned, the program in Phase II aims at further improvement in the performance of large-scale cells, including safety issues in battery modules using these high-performance large-scale cells, and the formulation of road maps towards the worldwide dissemination of large-scale lithium ion secondary batteries. In addition to these R&D programs, a new target has been presented for the earlier practical application of several kilowatt hour (kWh) class battery modules [1]. Two types of battery modules have been developed, i.e. those for applications in stationary devices and those for electric

vehicles. Cathode materials for these cells are either nickel–cobalt (Ni–Co) oxides or manganese (Mn) oxides. It is considered that they should have the performance targets as shown in Table 1.

The batteries developed in this project have satisfied the performance requirements.

2. Selection of materials and their combination by rule of thumb

In order to improve the performance of cells and battery modules in Phase II, the following items, including battery materials, battery shape, and safety measures, have been taken into consideration.

2.1. Cathode materials

As Co is expensive and not abundant in nature, LiCoO_2 is not desirable to be applied to cathode-active material for large-scale lithium batteries with a great amount of uses expected. Thus, instead of Co, metals in the same transition series such as Ni and Mn are used as lithium oxide.

2.2. Anode materials

Carbon complex anode materials which have longer life and higher capacity than the single graphite anode

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Table 1

Target and results of battery modules performance evaluation tests (achieved in FY1998)

R&D target	Stationary type		EV application type	
	Test results		R&D target	Test results
	Ni–Co battery system (cylindrical cell shape)	Mn battery system (prismatic cell shape)		
Capacity (kWh)	2	2.14	2.04	3
Specific energy (Wh/kg)	120	116	100	3.55
Energy density (Wh/l)	240	174	213	107
Specific power (W/kg) ^a			300	198
Energy efficiency (%)	90	96.7	400	416
Cycle life (cycles)	3500	In progress	85	96.6
			1000	In progress
				In progress

^a Specific power was calculated from V – I characteristics and cut-off voltage at 80% DOD.

used in small-scale lithium batteries in Phase I are to be developed.

2.3. Electrolytes

To improve the charging–discharging behavior and cycle life, supporting electrolytes and the composition of solvents have to be optimized by considering the combination of cathode- and anode-active materials.

2.4. Separators

Considering the effects of a separator not only on the charging–discharging behavior but also on the safety, the material properties of the separator as well as the pore size should be optimized.

2.5. Materials and shapes of capsules

Various improvements in the fabrication of cells, such as materials to be used and method of fabrication, will be made.

2.6. Safety considerations

Safety improvements in the cell component materials, safety design of cells, and external protection circuits have to be optimized.

3. Materials and their quality improvement

In this section, the improvement of both cathode- and anode-active materials is to be introduced.

3.1. Cathode materials

Cells in which Co is substituted by Ni or Mn have been developed.

3.1.1. Ni–Co system

The effective-capacity density of LiNiO_2 is approximately 20% greater than that of LiCoO_2 . However, the crystal structure of LiNiO_2 is broken by the repetitive charging and discharging, which results in a significant drop in capacity.

Thus, by substituting some Ni by Co or other elements, the breakdown of the crystal structure due to charging–discharging cycles can be suppressed. The crystallization of the active substances can be improved by this substitution and by improving the synthetic method.

Using various Ni–Co compound oxides, charging–discharging cycle characteristics were investigated as shown in Fig. 1. $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ proved to have the highest specific capacity of more than 150 Ah/kg. In addition, the composition had excellent charging–discharging cycle characteristics [2].

LiNiO_2 is not advantageous in terms of safety, because its thermal decomposition temperature is low and the amount of heat generated during decomposition is large. The substitution of Ni by Co resulted in the increase in the exothermic peak temperature from approximate 211°C of LiNiO_2 to about 218°C at a Co concentration of 23% [1].

It was elucidated from thermal tests that the thermal decomposition temperature increased, when Al is added to the Ni–Co compound oxide. Fig. 2 shows the effect of the amount of Al on the thermal decomposition temperature.

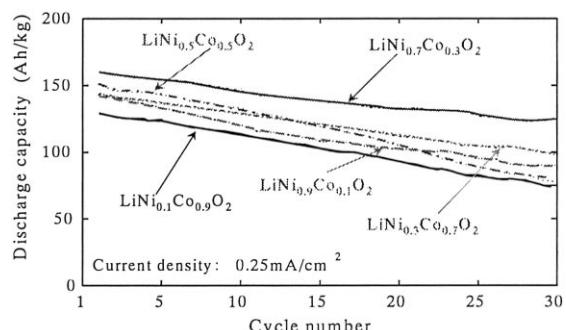


Fig. 1. Cycle performance of several $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode.

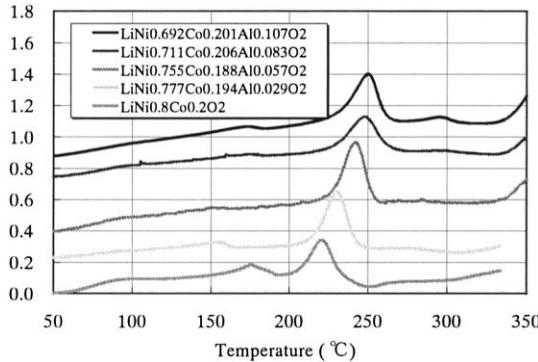


Fig. 2. DSC curves of Ni–Co system with Al addition (at 4.4 V charge).

When 11% Al was added, the peak temperature for thermal decomposition increased to 250 from 220°C, though its capacity decreased.

3.1.2. Mn system

The effective-capacity density of LiMn_2O_4 is approximately 20% lower than that of LiCoO_2 , but LiMn_2O_4 is expected to have high thermal stability and to reduce the price of the battery. However, because the volume change of LiMn_2O_4 with the stoichiometric composition ($\text{Li}/\text{Mn} = 0.5$) is large during charging and discharging, the cycle life is short.

To increase the cycle life by reducing the volume change of the lattice structure, the crystal structure was stabilized through synthesizing a Li-rich LiMn_2O_4 compound in which atomic ratio Li/Mn is higher than the stoichiometric value of 0.5.

In a cycle life test using single electrode tests, Li-rich Mn cathode has extended the cycle life from 500 to 2500 cycles, as shown in Fig. 3. It was obtained by optimizing the Li to Mn ratio and the baking conditions, under such conditions that the capacity maintains 70% or more of the initial capacity.

3.2. Anode materials

Through the improvement of carbon materials, the performance of the carbon anode was improved.

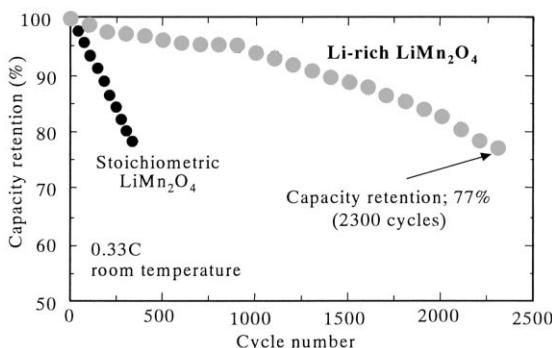


Fig. 3. Cycle life performance of Li-rich LiMn_2O_4 cathode.

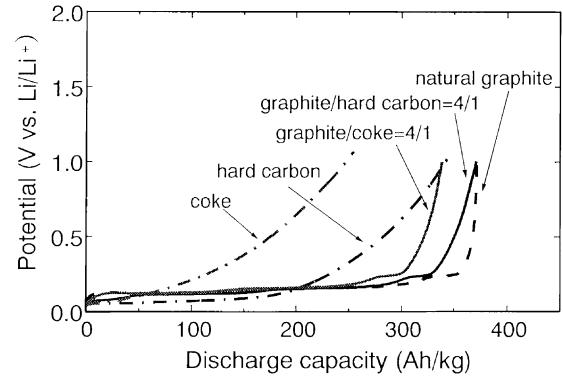


Fig. 4. Discharge curves of several carbon anodes.

3.2.1. Graphite–coke hybrid anode

With a natural graphite single electrode, a sharp potential change is observed towards the end of discharge, and side reactions between graphite and electrolyte tend to occur because of the irregular potential distribution on the electrode. This is disadvantageous to the longevity of the electrode. To solve this problem, carbon compound anodes which have a longer cycle life than the graphite anode were developed.

A graphite–coke hybrid electrode, which consists of coke mixed with natural graphite, has been developed. The coke used was a low crystallization carbon with relatively mild potential variation during discharge. Though the discharge capacity of the graphite–coke hybrid is lower than that of natural graphite only, the potential variation occurring towards the end of discharge was reduced, as shown in Fig. 4. It gives discharge characteristics of several carbon negative electrodes.

3.2.2. Ag-dispersed graphite anode

When LiMn_2O_4 cathode whose capacity density is lower than that of LiCoO_2 is used, a measure to increase the capacity of the anode must be adopted to increase the overall energy density of the battery.

To improve the electrical conductivity between neighboring graphite particles and to increase the capacity of the anode, Ag-dispersed graphite anode was developed [3]. Massive graphite has a better packing property, a higher capacity, and less side reactions with electrolyte than the scale type graphite used conventionally. Ag which forms LiAg alloy with Li deposited as microparticles on the graphite surface using a wet chemical reduction.

The following points were clarified by single-electrode tests, as shown in Fig. 5. As a result of Ag dispersion, the initial specific capacity was improved by approximately 10% to 800 Ah/l and the cycle life was improved substantially from 200 to 4200 cycles under the conditions that the capacity maintains 70% or more of the initial capacity.

3.2.3. Graphite-hard carbon hybrid anode

To improve the cycle life and alleviate potential variations towards the end of the discharge of a battery, a graphite-hard

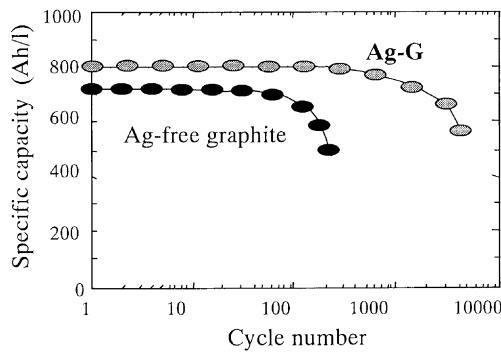


Fig. 5. Volumetric capacity densities of Ag-G and Ag-free graphite anodes.

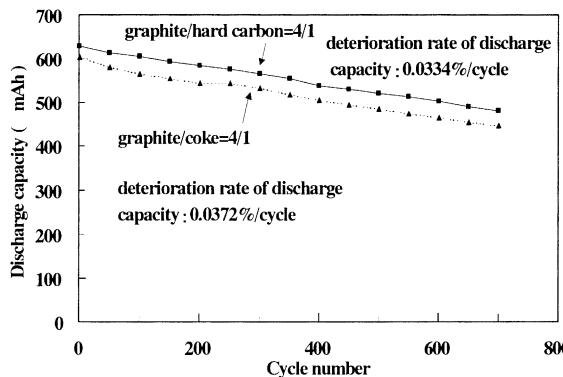


Fig. 6. Cycle performance of 2 Wh class cell using graphite-hard carbon and graphite-coke hybrid anodes.

carbon hybrid anode has been developed. It possesses a high discharge capacity and does not react with electrolyte solutions easily [4].

Fig. 6 shows cycle performance obtained for 2 Wh class cells. The graphite-hard carbon hybrid electrode provided a discharge capacity close to that obtained by a battery using a graphite-only electrode (approximately 370 Ah/kg). The graphite-hard carbon hybrid anode presented higher capacity and longer cycle life characteristics than those of the graphite-coke hybrid anode.

4. Characteristics of the batteries developed

Exterior views of the four battery modules developed in this project are shown in Fig. 7 with their respective material composition and shape. LIBES has developed two types of modules (Ni–Co and Mn systems) each for stationary device and electric vehicles (EV) applications. Each module consists of eight cells connected in series. The structures of these cells include cylindrical, elliptic cylindrical, and prismatic types.

Newly developed cells and battery modules based on the above-mentioned R&D procedures are compared in terms of

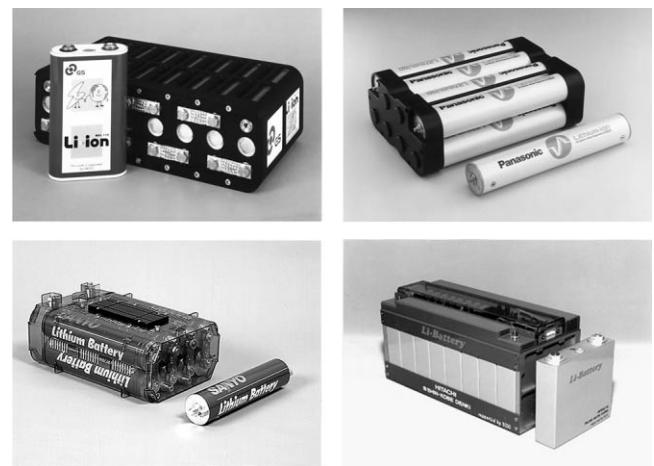


Fig. 7. Battery modules developed in the project.

their short-term and long-term performances. Currently, further improvements in energy density and the cycle life of the cells themselves are being pursued. For that purpose, the materials for cathodes and anodes, the shapes and structures for batteries, and the methods for cell connections are being investigated repeatedly.

4.1. Electric performances

Table 1 summarizes the results of the performance of stationary and EV application type modules obtained thus far.

Original target parameters such as battery capacity and energy efficiency have already achieved their original targets for both types. Specific power has also reached its target in the battery module level for the purpose of electric vehicle application.

4.2. Long-term performances

In this section, the long-term characteristics, namely, the cycle life characteristics, are introduced.

The evaluation of cycle life has been performed on single electrodes, small cells, cells used for the development of large-scale cells and modules. Since cells were improved every year, cycle life tests have been performed every time new cells were developed using cells and modules fabricated on the basis of the most recently available specifications.

Figs. 8 and 9 show the cycle life characteristics of a Mn system stationary type 250 Wh class cell and a Ni–Co system 3 kWh class battery module for EV application, respectively.

Life-cycle tests on the four types of cells and modules are now being continued. A total of 700 and 600 cycles were reached for the Mn system stationary type and the Ni–Co system EV application type, respectively, as of 1 March 2000.

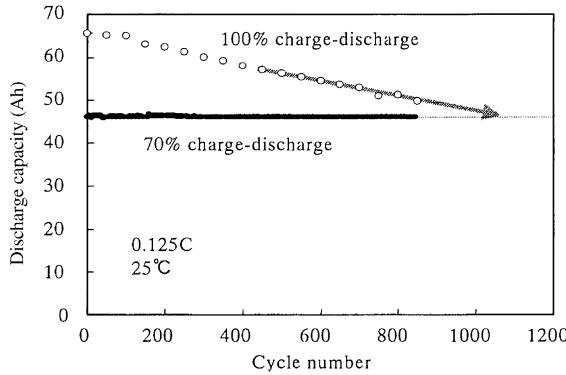


Fig. 8. Cycle life performance of 250 Wh class cell using Ag-G anode and Li-rich LiMn_2O_4 cathode.

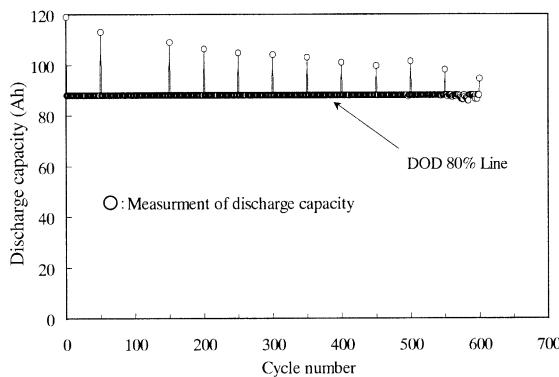


Fig. 9. Cycle life of the Ni-Co system battery module.

5. Possible applications for medium-sized lithium battery packs

Since FY1998, the development of medium-capacity battery systems for small- and medium-sized electric vehicles as well as for demand-side stationary device applications has been underway. This new development is not only based on the results for large-scale cells and battery modules obtained thus far, but also aims at further performance improvements of the battery systems. In Phase II, this project is expected to realize earlier practical applications of lithium secondary batteries.

6. Conclusions

1. By substituting Co with Ni or Mn, cathodes which have high-capacity density and long cycle life have been developed for use in large-capacity lithium ion secondary batteries, such as $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$ with capacity of more than 150 Ah/kg and Li-rich LiMn_2O_4 with cycle life of 2500 cycles.
2. By searching for anodes with high capacity and long cycle life, anodes whose performance exceeds that of a graphite-only anode, such as the graphite–carbon hybrid anode with reduced potential variation near the end of discharge, and the Ag-dispersed graphite anode with specific capacity of 800 Ah/l and cycle life of 4200 cycles, have been developed.
3. Through the improvement of the performance of materials and structural-level characteristics, high-energy density, long life, and large-capacity lithium ion cells and modules have been developed. Original targets of stationary type modules (2 kWh of capacity, 90% of energy efficiency) and of EV application type modules (3 kWh of capacity, 400 W/kg of specific power, 85% of energy efficiency) have been achieved.

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References

- [1] T. Iwahori, Y. Ozaki, A. Funahashi, H. Momose, I. Mitsuishi, S. Shiraga, S. Yoshitake, H. Awata, *J. Power Sources* 8–82 (1999) 872–876.
- [2] I. Yonezu, T. Maeda, Y. Chikano, K. Ohkita, H. Kurokawa, T. Nohma, K. Nishio, *Dialogue Session 2, Batteries 7.5, EVS-15*, 1998.
- [3] K. Nishimura, N. Nakajima, Y. Ozaki, S. Taniguchi, S. Arai, H. Awata, T. Iwahori, A. Fukutome, *Abstract no. 380, ECS 196*, 1999.
- [4] A. Funahashi, K. Yanagida, A. Yanai, T. Maeda, K. Ohkita, Y. Chikano, T. Nohma, I. Yonezu, *Abstract no. 377, ECS 196*, 1999.